

## Analysis of Plasma-Nitrided Steels

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## ANALYSIS OF PLASMA-NITRIDED STEELS

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### SUMMARY

The analysis of plasma nitrided steels can be divided to two main categories - structural and chemical. Structural analysis can provide information not only on the hardening mechanisms but also on the fundamental processes involved. Chemical analysis can be used to study the kinetics of the nitriding process and its mechanisms. In this paper preliminary results obtained by several techniques of both categories are presented and the applicability of those techniques to the analysis of plasma-nitrided steels is discussed.

### INTRODUCTION

Product analysis has an important roll in many operations. In the industry it is essential to quality control and trouble shooting. From the scientific aspect it can yield valuable information about the fundamental processes involved. This seems to be especially important in the field of plasma chemistry where even the basic principles are yet to be well understood and very few efficient research tools are available. Even the mechanisms involved in plasma nitriding, which is one of the simplest plasma operations, are still subject to myths, rules of thumb, and irrational hypotheses. These reasons prompted us to devote effort to the analysis of plasma-nitrided steels. This work is in its very early stages, though, and thus what we are going to present here is just some preliminary results and a few guidelines to further progress in this area.

The traditional analytical procedure used in both industry and research is determination of the case depth. This is done by cross-sectioning a sample of the nitrided material and measuring the hardness along a line. This method is destructive and requires considerable work. An example demonstrating it is presented in fig. 1 taken from the Metals Handbook (ref. 1). Although this method has been instrumental in the study of the kinetics and efficiency of nitriding processes for many years, the information it provides is limited. Today many analytical techniques are available which can give a much broader picture.

The analysis of nitrided steels can be divided to two main categories - structural and chemical. Structural analysis can yield valuable information about the phases formed as a result of nitriding and their distribution. This, in turn, may shed light not only on the hardening mechanisms but also on the fundamental processes involved. Chemical analysis, on the other hand, is expected to provide information concerning the kinetics and mechanisms of these processes. Such information, besides its scientific value, may lead to improvements in industrial nitriding operations.

## STRUCTURAL ANALYSIS

The basic technique of structural analysis is x-ray diffraction (XRD). A diffraction pattern obtained from a 4140 steel sample which was nitrided by means of a glow discharge process is shown in figure 2, where a diffractogram obtained from an as-received sample of the same material is also shown for comparison. These diffractograms enable us to identify the phases formed in the process. Thus, it is seen that in this case the nitriding results in the formation of the two iron nitrides -  $\text{Fe}_{2-3}\text{N}$  and  $\text{Fe}_4\text{N}$ ; presence and intensities of these nitride peaks is closely related to an important technical factor, namely the white layer, which is undesirable for most applications. It is now well established that it is this layer which contains those nitrides. This is demonstrated in figs. 3 and 4 which show respectively a metallograph and a diffraction pattern obtained from a supernitralloy sample which was nitrided by means of the recently developed ion-beam nitriding process (ref. 2). As can be seen no white layer is formed in this process and consequently no iron nitride peaks are present in the diffractogram. Thus, x-ray diffraction can serve as a non-destructive technique for determining the presence or, after proper calibration, the thickness of the white layer.

This, however, is not the only information which can be derived from x-ray diffraction. Closer examination of the diffractograms in figs. 2 and 4 reveals that in both cases the nitriding resulted in the disappearance of some of the diffraction lines of iron such as (200) and (220). This implies that the nitriding has also caused some structural change in the iron matrix. The nature of this structural change is not known yet but it seems that other analytical techniques such as electron microscopy may resolve this.

## CHEMICAL ANALYSIS

### Auger Electron Spectroscopy

Nitriding is a surface process and it is therefore natural to employ for its study one of the numerous surface analytical techniques developed in the last two decades (ref. 3). Among these the most established one is Auger electron spectroscopy (AES). This technique is very powerful in providing information on the elemental composition of surface layers. Auger spectra of supernitralloy in the as-received state and following nitriding by means of the ion-beam technique are given in figure 5, where the nitrogen peak resulting from the nitriding is clearly seen.

Unfortunately, however, very little information can be readily derived from these spectra. This is due to two features of the Auger technique. First, although the intensity of the various peaks in an Auger spectrum depends on the concentrations of the corresponding elements, there is no simple method of translating these intensities to absolute concentrations, and calibration with samples of known compositions is necessary. The Auger technique is also not very helpful in obtaining the other parameter in which we are interested, namely the distribution of nitrogen in the sample. This is due to the fact that the Auger signal comes from the very few (usually not more than 10) outermost atomic layers whereas the thickness of the nitrided layer is of the order of microns. We tried to overcome this problem by means of depth profiling using the sputter-etching technique. Yet, even after several hours of sputter-etching no change in the intensity of the nitrogen peak was observed.

### Rutherford Back Scattering

The obvious way to overcome this limitation of AES is by using an analytical method which is not limited to few surface layers but is capable of providing information about the composition of deeper layers as well. One such method is Rutherford back-scattering (RBS)(ref. 4). In the RBS technique the sample surface is bombarded with light ions which were accelerated to kinetic energies of hundreds or even thousands of KeV. This results in penetration depth of the order of microns and thus this technique seems to ideally suit our needs.

RBS spectra of as-received and ion-beam nitrided samples of supernitralloy (actually, the same samples that were used for AES) are presented in figure 6. One can readily see the main shortcoming of the RBS technique in our case, namely its insensitivity to nitrogen. The reason for this is that the RBS signal of an element depends on its scattering cross-section which, in turn, is proportional to the square of its atomic number. This is unfortunate in situations such as ours where one wishes to determine the concentration of a light element (nitrogen in our case) in a matrix of a much heavier one (in our case iron) since the signal due to the former is masked by that due to the latter. A possible solution to this problem may be the use of another analytic technique, related to RBS, which is known as nuclear reaction analysis.

### Energy-Dispersive X-ray Analysis

Having failed to obtain quantitative results by means of the AES and RBS techniques we turned to yet another analytical method which was available to us - energy-dispersive x-ray analysis (EDS). In this technique, like in AES, electrons are accelerated towards the sample surface. In the case of EDS, however, one detects the x-rays emitted from the surface as opposed to the slow Auger electrons which one detects in AES. Since the absorption of x-rays by the sample is much less than the absorption of the Auger electrons, the depth analyzed by EDS is much greater, namely of the order of microns. It should be pointed out that due to the low atomic number of nitrogen its analysis requires that the EDS analyzer include light element capability. Many laboratories already have this capability.

EDS spectra of 4140 steel both as-received and following nitriding by means of a glow discharge process are presented in figure 7. At first the results look disappointing - it seems almost impossible to even detect the nitrogen peak, let alone measure its intensity. Standard programs supplied

with the analyzer allow us to examine difference spectra. Thus, we can subtract the two spectra of figure 7 from each other after adjusting the height of the iron peak in both of them and obtain the difference spectrum. The result is shown in figure 8, and as can be seen it allows us to measure the area underneath the nitrogen peak and thus have a quantitative measure of the amount of nitrogen in the sample. This clears the way to kinematic studies of nitriding processes.

Another way in which the EDS technique can be used is mapping. An example of a SEM micrograph of 4140 steel nitrided by means of a glow discharge process alongside the corresponding nitrogen map is shown in figure 9. This map can be easily utilized to determine the nitrogen distribution in the sample.

### CONCLUSIONS

Both structural and chemical analyses are capable of providing important information about the mechanisms involved in nitriding of steels. For chemical analysis energy-dispersive x-ray analysis seems to have the greatest potential while electron microscopy is probably the most promising structural analysis technique.

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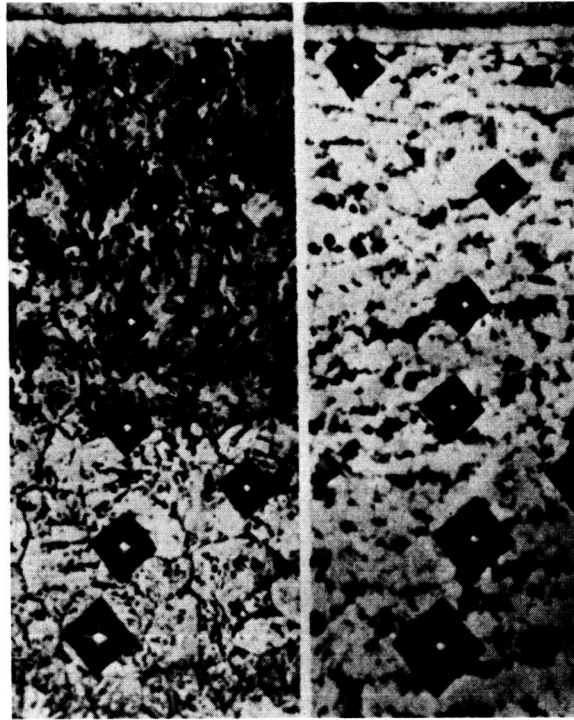


FIGURE 1. - CASE DEPTH DETERMINATION BY MEANS OF HARD-  
NESS MEASUREMENTS (FROM REF. 1).

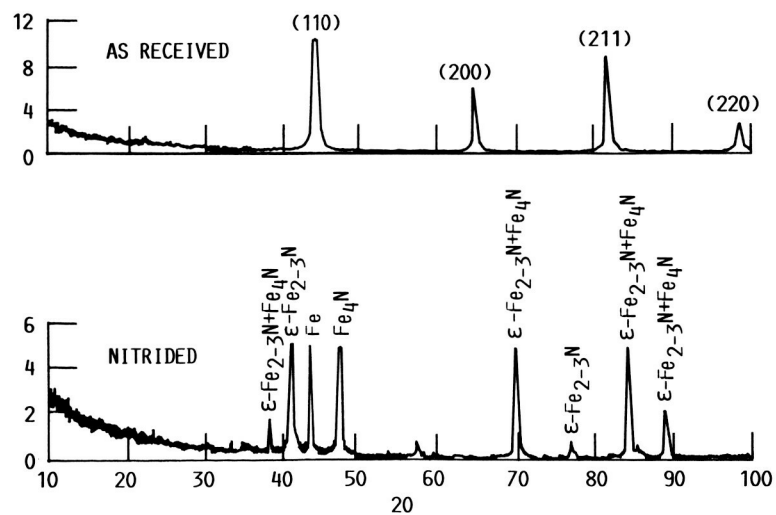


FIGURE 2. - X-RAY DIFFRACTION PATTERN OBTAINED FROM 4140 STEEL  
NITRIDED BY A GLOW-DISCHARGE PROCESS.

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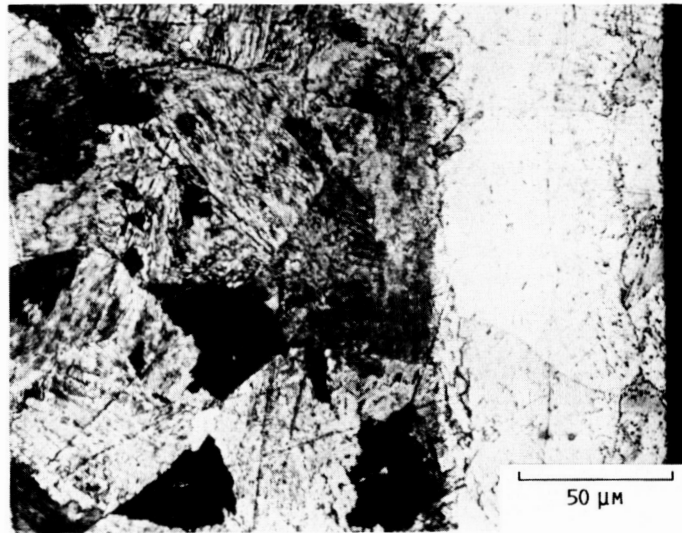


FIGURE 3. - MICROGRAPH OF SUPERNITRALLOY NITRIDED BY THE ION-BEAM PROCESS.

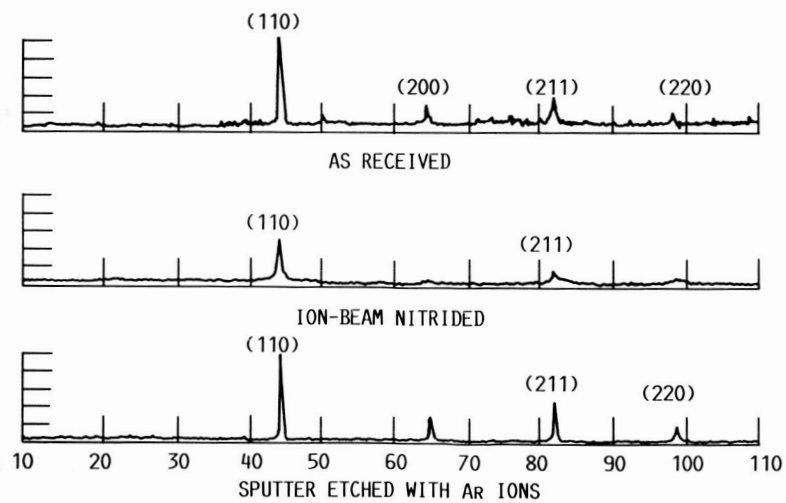
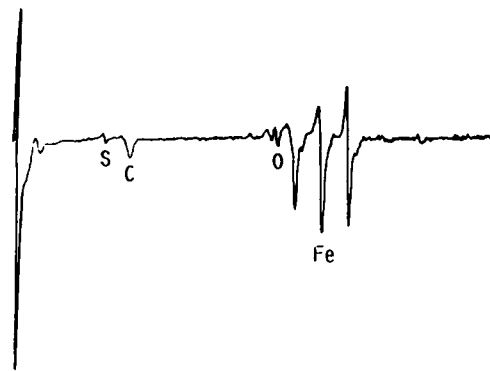
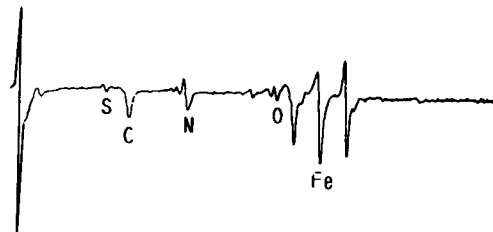


FIGURE 4. - DIFFRACTOGRAM OBTAINED FROM ION-BEAM NITRIDED SUPERNITRALLOY.



AS RECEIVED



NITRIDED

FIGURE 5. - AUGER SPECTRA OF AS-RECEIVED AND ION-BEAM NITRIDED SUPERNITRALLOY.

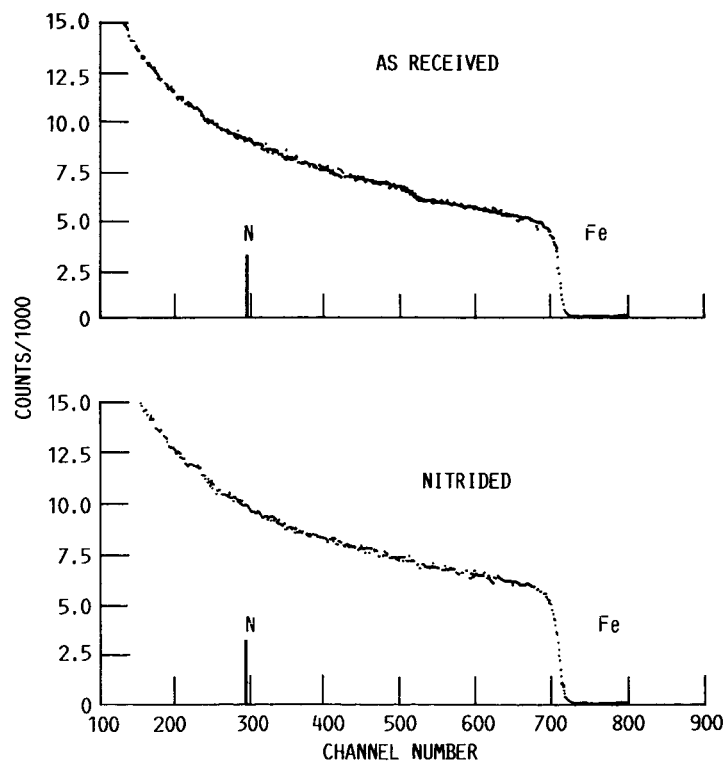


FIGURE 6. - RBS SPECTRA OF AS-RECEIVED AND ION-BEAM NITRIDED SUPERNITRALLOY.



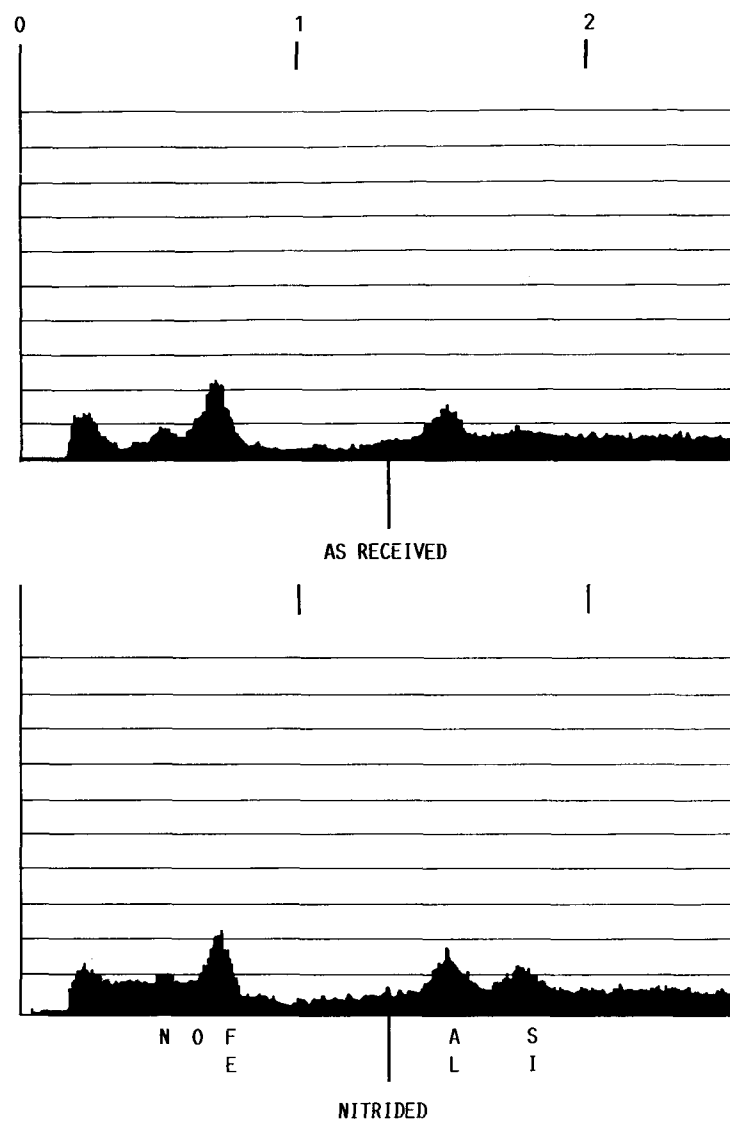


FIGURE 7. - EDS SPECTRA OF AS-RECEIVED AND PLASMA-NITRIDED 4140 STEEL.

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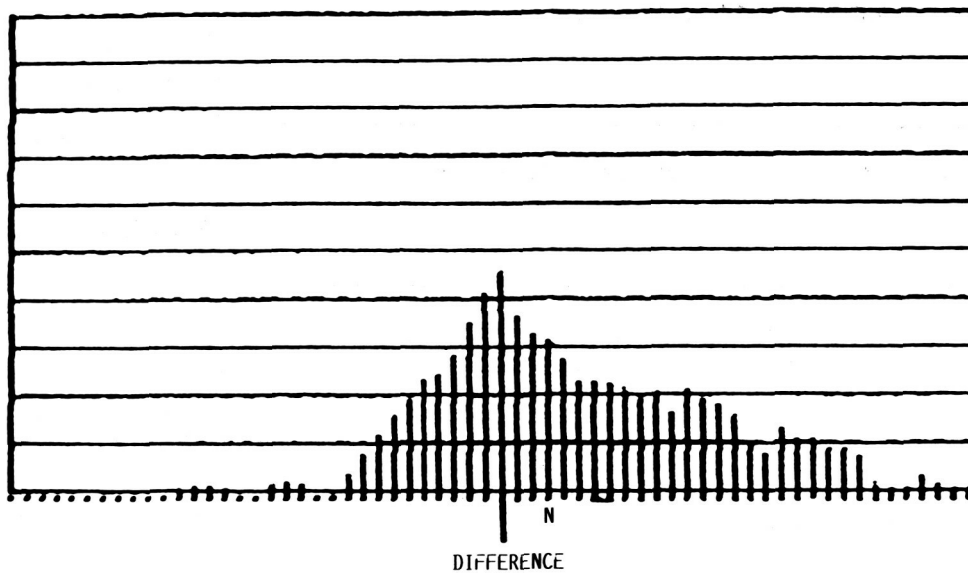


FIGURE 8. - SPECTRUM OBTAINED BY SUBTRACTION OF THE TWO SPECTRA OF FIGURE 7.

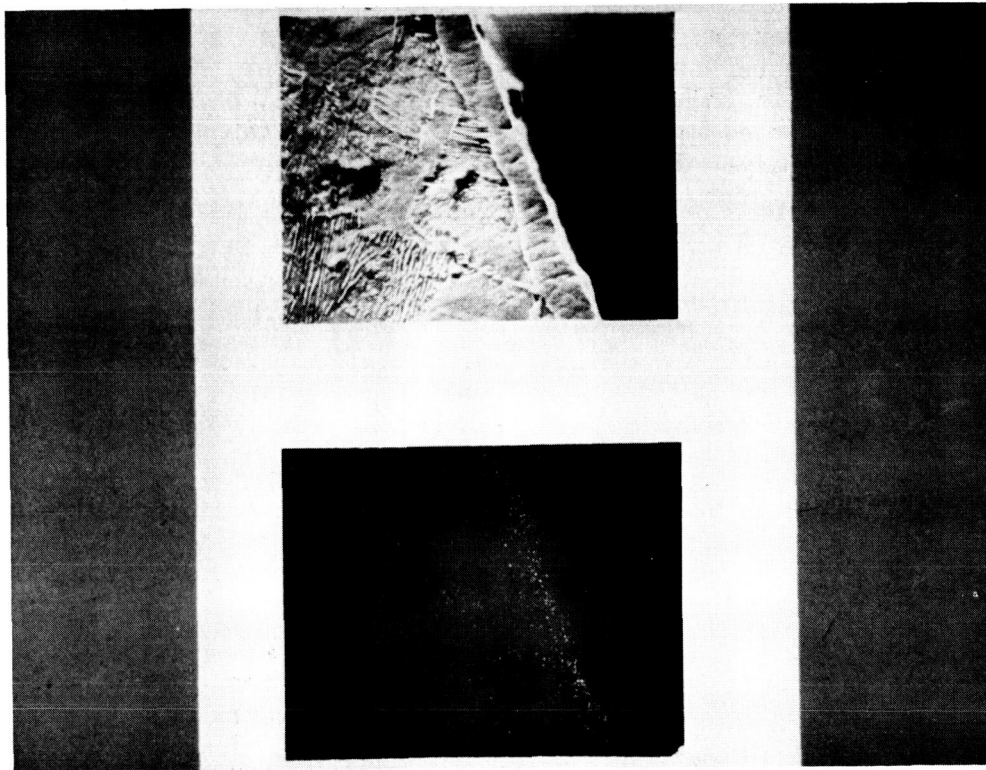


FIGURE 9. - SEM MICROGRAPH AND NITROGEN MAP OF PLASMA-NITRIDED 4140 STEEL.

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